Polyisocyanuratoesters: Renewable Linear Polyesters with High Flame Retardancy

Zijian Chen[1], Rui Hou, Jianbing Cheng, Fengjie Fang, Donglin Tang*, Guangzhao Zhang

School of Materials Science and Engineering, South China University of Technology, 381 Wushan Road, Tianhe District, Guangzhou 510640, P. R. China

ABSTRACT: Biobased urea nowadays attracts increasing attention as a biomass resource with giant potential, which benefits from the development of biobased ammonia and ecological sanitation system. Urea is an ideal feedstock for chemical industry and developing new urea-based polymer materials can take advantage of the urea resource. In this work, a class of renewable linear polyesters, namely polyisocyanuratoesters (PICEs) were synthesized from a urea-based monomer bis(2-carbomethoxyethyl) isocyanurate and biobased aliphatic diols. Compared with conventional aliphatic polyesters, PICEs containing isocyanurate rings in the polymer chain backbone exhibit outstanding flame retardancy that both PICE-4 (the number '4' refers to the number of methylene in diols, e.g. 4 for butylene and 6 for hexylene) and PICE-6 have high limiting oxygen index values over 30%. In the UL 94 tests, PICE-6 reaches V-1 rating; while V-2 is found for PICE-10. All PICEs exhibit similar pyrolysis behavior that the temperatures of 5% weight loss are around 320°C. PICEs are found to have glass transition among 20°C-45°C. No crystallization behavior is observed without annealing except for PICE-10, which can crystallize even at room temperature.

KEYWORDS: Urea, isocyanurate ring, aliphatic diol, linear polyester, flame retardancy.

1 INTRODUCTION

Urea is a special organic compound containing both amino group and carbonyl group, which can form abundant derivatives as an ideal feedstock for chemical industry for safety (non-flammable and practically non-toxic) and low cost [1, 2]. Urea is mainly synthesized from synthetic ammonia industry [3], but the ammonia can be also produced from renewable biomass resources (Scheme 1) for the reduction of CO_2 emission [4, 5]. Additionally, the manufacture of urea is the largest scale of chemical fixation of CO_2, which is beneficial to both environment and economy [6]. Furthermore, since urea is an ingredient of human urine [7], the sewage of urine is a huge biomass resource to produce urea. In recent years, a new kind of sewage treatment system called ecological sanitation system has been developing rapidly and popularize world, which provides an efficient route to recycle urea and ammonia from urine [8-10]. Recycling urea from sewage can not only take advantage of the biobased urea resource but also reduce eutrophication [11]. Therefore, urea is a promising biomass resource and developing new urea-based polymer materials can take advantage of this resource.

Isocyanuric acid is one of the most important derivatives of urea, which can be synthesized via trimerization of urea [12]. Isocyanuric acid and its derivatives are thermally stable due to the isocyanurate ring structure [13-15], and some of them such as melamine cyanurate and tris (2, 3-dibromopropyl) isocyanurate are effective flame retardants. Polyisocyanurate (PIR) is a category of polymers containing isocyanurate linkages. The existence of isocyanurate moieties offers PIRs outstanding chemical and thermal stability and flame retardancy, thus they have been widely used as elastomers, resins and rigid foams [16, 17]. However, these materials are thermosetting since they are prepared by the trimerization of isocyanates [17] or by the crosslinking reaction of isocyanuric acid or its trifunctional derivatives [18], which limits their processing and applications. Meanwhile, flexible segments have to be introduced in PIR materials to improve the mechanical properties since the pure PIR is brittle [17]. By comparison, studies on linear polymers containing isocyanurate rings are fewer [19, 20] since difunctional isocyanurate derivatives are difficult to be prepared. Nevertheless, Frazier and coworkers [21] developed a route to synthesize one of the disubstituted isocyanurates, bis(2-carboxyethyl) isocyanurate (BCI) from isocyanuric acid simply by Michael addition and hydrolysis. Since the BCI molecule contains two carboxylic acid groups, BCI and its ester derivative, namely bis(2-carbomethoxyethyl) isocyanurate (BCMI), are suitable for synthesizing linear polyesters.

Many aliphatic diols are manufactured from

584 *J. Renew. Mater.*, Vol. 6, No. 6, October 2018

© 2018 Tech Science Press

biomass resource, e.g.1,4-butanediol (BDO) [22, 23] and 1,6-hexanediol (HDO) [24-26] can be produced from sugar while 1,10-decanediol (DDO) [27] can be synthesized from castor oil. They are promising biobased platform chemicals and have been widely used as monomers to produce polyesters. However, most of the polyesters are combustible. Therefore, they need to be blended with flame retardants to improve their flame retardancy when they are used in some applications such as plastic conduit pipe and fabric [28, 29]. In this work, a series of renewable linear polyesters, namely polyisocyanuratoesters (PICEs), are proposed in order to take advantage of the biomass resource of both urea and aliphatic diols (Scheme 1).
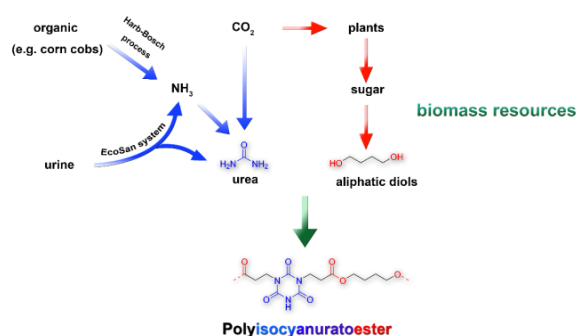
Scheme 1 Strategy of synthesizing PICEs from biomass resources.
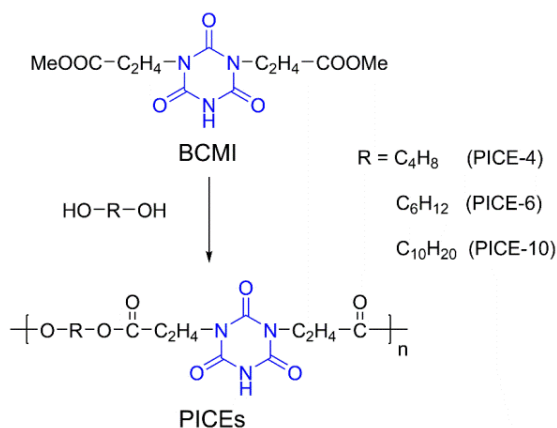
Scheme 2 Synthesis of PICEs from BCMI.

These polymers are designed to be synthesized via transesterification polymerization of BCMI and aliphatic diols, including BDO, HDO and DDO (Scheme 2). The nomenclature of polymers here starts with 'PICE' and ends with a number corresponding to the number of methylene groups in diols, e.g. 4 for butylene, 6 for hexylene and 10 for decylene. The

isocyanurate linkages introduced to the polymer backbone are supposed to provide PICEs with strength and good thermal stability. The aliphatic segments of PICEs endow the polymer chains with flexibility. Furthermore, the isocyanuarate ring structure is also supposed to offer PICEs with high flame retardancy without adding flame retardants.

2 EXPERIMENTAL

2.1 Materials

1,4-Butanediol (BDO, 99%), 1,6-hexanediol (HDO, 98%) and 1,10-decanediol (DDO, 98%) were purchased from Aladdin Industrial Corporation (Shanghai, China). Bis(2-carboxyethyl) isocyanurate (BCI, 98%) and titanium(IV) butoxide (TBO, 98%) were bought from Energy Chemical Corporation (Shanghai, China). *N*, *N*-Dimethylformamide (DMF, AR) was purchased from Chinasun Specialty Products Corporation (Jiangsu, China). Hexane (AR), was bought from Sinopharm Chemical Reagent Corporation (Shanghai, China). Hydrochloric acid (AR, 36-38 wt%) was purchased from Guangzhou Chemical Reagent Factory (Guangzhou, China) and methanol (AR) was from Guangzhou Donghong Industrial Development Corporation (Guangzhou, China). Dimethyl sulfoxide-*d*6 (DMSO-*d*6, 99.9%, containing 0.03% tetramethylsilane) was bought from Cambridge Isotope Laboratories, Inc. (MA, USA). BDO and HDO were purified by vacuum distillation while DDO and TBO were dried *in vacuo* before use. The other chemicals mentioned above were used as received without further treatment.

2.2 Characterizations

[1]H- and ^{13}C-nuclear magnetic resonance (NMR) were detected at 25ºC on a Bruker AVANCE III HD 600 (600 MHz) spectrometer (Germany) and chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard (DMSO-*d*6: δ 2.50 ppm). Thermogravimetric analysis (TGA) was conducted on a Netzsch TG 209 F3 Tarsus instrument (Germany) at a heating rate of 10 °C/min under nitrogen atmosphere (50 mL/min). Differential scanning calorimetry (DSC) was carried out at a heating rate of 20 °C/min and a cooling rate of 10 °C/min using a Netzsch DSC 204 F1 (Germany). The limiting oxygen index (LOI) was tested according to GB/T2406.2-2009 (specimen size: 80 mm×10 mm×4 mm) on a FTT0077 oxygen index instrument (Fire Testing Technology Co. Ltd., UK). The vertical burning test was carried out on a FTT0082 UL94 flame chamber (Fire Testing Technology Co. Ltd., UK) according to the standard UL 94-2009 (specimen size: 130 mm×13 mm×4 mm).

2.3 Synthesis of Bis(2-carbomethoxyethyl) Isocyanurate (BCMI)

BCI (54.6 g, 0.2 mmol) was added into methanol (400 mL) with concentrated HCl (33.3 mL, 0.4 mol). The slurry was refluxed at 70°C for 1 h and it generally turned into clear solution. White crystal precipitated out when the solution cooled down to room temperature. After filtration and washing with cold methanol, the residue was collected and dried *in vacuo* at 100°C overnight. 48.4 g product (yield: 80%) was obtained.

^{1}H-NMR (600 MHz, DMSO-$d6$, δ): 11.80 ppm (s, 1H, NH), 3.92 (t, 4H, NCH_2), 3.59 (s, 6H, OCH_3), 2.57 (t, 4H, CH_2CO); ^{13}C-NMR (600 MHz, DMSO-$d6$, δ): 171.17 ppm (COO), 149.71 (NCON), 148.59 (NHCO), 51.65 (CH$_3$), 37.37 (NCH$_2$), 31.83 (CH$_2$CO).

2.4 Synthesis of polyisocyanuratoesters (PICEs)

A series of PICEs, including PICE-4, PICE-6 and PICE-10, were prepared in a similar procedure. BCMI (15.6 g, 50 mmol), aliphatic diol (100 mmol for BDO or HDO while 55 mmol for DDO) and TBO (50 mg) were added into a three-neck flask equipped with an argon inlet, mechanical stirrer and Vigreux column connected to a Dean-Stark trap. The reaction was performed at 170°C for 6 h with stirring under argon to form oligomers, then vacuum was applied and the temperature was gradually raised to 190°C and kept for 6 h-12 h (for PICE-4, kept at 170°C). When the polymerization finished, DMF was added to dissolve the crude polymer and then precipitated in hexane. After filtration and washed with hexane, the residue was collected and dried *in vacuo* at 70°C overnight to obtain final product.

3 RESULTS AND DISCUSSION

3.1 Synthesis of PICEs

Polyisocyanuratoesters (PICEs) were prepared via transesterification polymerization from bis (2-carbomethoxyethyl) isocyanurate (BCMI) and different aliphatic diols (DOs).

Comparing with bis(2-carboxyethyl) isocyanurate (BCI, m.p. 289°C [21]), BCMI has lower melting point (117°C [30]) and better solubility in DOs. The methods of esterification of acid-substituted isocyanurate derivatives have been reported [21, 30]. BCI gradually reacted with methanol to form BCMI and dissolved. It took about 30 min for the slurry to turn into clear solution and all the BCI converted to BCMI after 1 h. BCMI precipitated when the solution was cooled to room temperature, which is convenient to obtain pure product by filtration.

The polycondensation system was first heated at 170°C for 6 h to form oligomers. Since 1,4-butanediol (BDO) and 1,6-hexanediol (HDO) are more volatile upon heating, the feed ratio of n(DO)/n(BCMI) was set to 2 to obtain hydroxy-terminated oligomers in the first step. The oligomers were then chain-extended by further transesterification under vacuum to obtain PICE-4 and PICE-6. For the synthesis of PICE-10, the boiling point of 1, 10-decanediol (DDO) is higher and it is less volatile so that the feed ratio of n(DDO)/n(BCMI) was set to be 1.1. It is worth noting that when the heating temperature was higher than 180°C during the synthesis of PICE-4, the product became elastic and insoluble. It is reported that the secondary amine can react with the hydroxy groups to form tertiary amine by the *N*-alkylation [31-34]. Therefore, PICE-4 is supposed to be crosslinked for the hydroxy groups reacted with the secondary amino groups of the isocyanurate rings in such a high temperature and vacuum condition. This phenomenon happened again even at 170°C when we tried to use ethanediol instead of BDO. However, for HDO and DDO, the polymers would not crosslink even heated at 190°C. When the polymerizations proceeded, the viscosity of polymers increased and Weissenberg effect was observed. Then the polymerizations were stopped for purification. From the ^{1}H-NMR spectra of the purified PICEs (see Figure 1), it is found that all the PICEs are hydroxy-terminated, and the number average molecular weight (M_n, see Table 1) can be calculated through the formula:

$M_n = (I_b + I_d) * M_{RU}/(2I_{e'})$

I_b, I_d and $I_{e'}$ are the integral of peak b, d and e' in NMR spectra, while M_{RU} means the molecular weight of the repeat units of PICEs. Gel permeation chromatography with DMF (contains 0.05 M LiBr) as an eluent was used to measure the weight average molecular weight (M_w) of PICEs, but no elution peaks were observed of the samples of PICEs, which is supposed that PICEs samples were adsorbed by the columns.
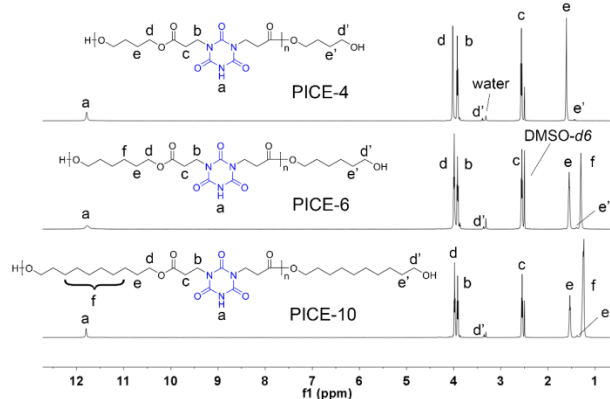
Figure 1 ^{1}H-NMR spectra (DMSO-$d6$) of PICE-4 (top), PICE-6 (middle) and PICE-10 (bottom).

Table 1 Properties of the PICEs.

Entry	DO	NMR	TGA		DSC
		$M_{n, NMR}$[a] (kg /mol)	$T_{d, 5\%}$[b] (°C)	$T_{d, max}$[c] (°C)	T_g (°C)
PICE-4	BDO	16.1	322.5	362.7	45.0
PICE-6	HDO	13.6	320.9	359.0	40.4
PICE-10	DDO	10.4	318.9	359.3	22.1

[a] The number average molar mass (M_n) was determined by the ^{1}H-NMR spectra (Figure 1);

[b] The temperature of 5% weight loss of samples;

[c] The temperature of maximum rate of weight loss.

3.2 Thermal Properties

The thermal stability of PICEs was studied by thermogravimetric analysis (TGA) and the results are shown in Table 1 and Figure 2. It has been reported that poly(lactic acid) [35, 36], poly(β-hydroxybutyric acid) [36], poly(ε-caprolactone) [36] and polyglycolide [37] have obvious weight loss below 300°C under nitrogen or helium atmosphere at a heating rate of 10 °C/min. Comparing with these typical aliphatic polyesters, PICEs show a relatively good thermal stability for there is no significant weight loss occurred below 300°C, which proves the introduction of isocyanurate rings can improve the thermal stability of aliphatic polyesters. When the temperature increases, all PICEs exhibit similar degradation behavior and we divide this process into two stages according to the previous reports [13, 14, 38]. First, the ester bonds in polymer chains dissociate and the aliphatic segments start to volatilize resulting in weight loss at about 320°C ($T_{d, 5\%}$ of PICE-4, PICE-6 and PICE-10 are 323°C, 321°C and 319°C respectively). The pyrolysis accelerates and the rate of weight loss reaches maximum at around

360°C as the DTG curves are shown in Figure 2(b) ($T_{d, max}$ of PICE-4, PICE-6 and PICE-10 are 363°C, 359°C and 359°C). When the temperature rises to about 380°C, the isocyanurate rings begin to pyrolyze resulting in the further weight loss. The weight loss of PICE-10 is slightly smaller than the one of PICE-4 and PICE-6 at the range of 360°C-430°C due to the longer aliphatic segment of PICE-10 is less volatile.

Both the glass transition temperature (T_g) and melting temperatures (T_m) of PICEs were also studied. The T_g of PICE-4, PICE-6 and PICE-10 are 45°C, 40°C and 22°C respectively from the results of differential scanning calorimetry (DSC, see Figure 3 and Table 1).
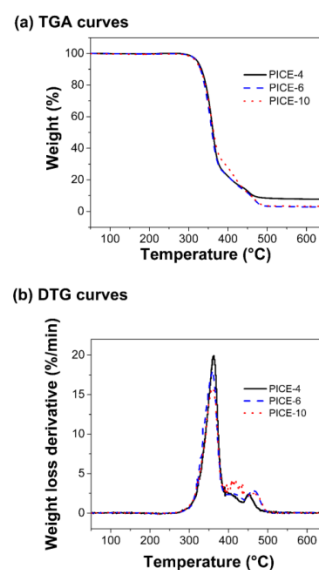

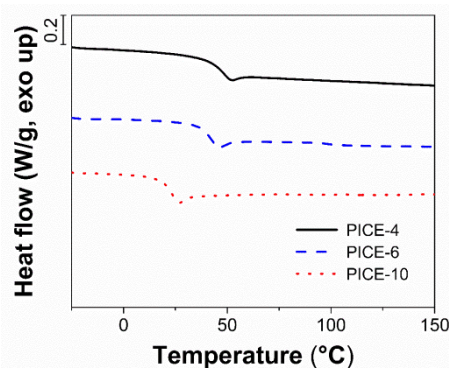**Figure 2** TGA curves and DTG curves of PICEs. (a) TGA curves (heating rate: 10 °C/min; nitrogen flow: 50 mL/min); (b) DTG curves.

Figure 3 DSC curves of PICEs. (2nd heating cycle with a heating rate of 20 °C/min).

One can see that T_g decreases when the number of methylene in PICEs increases from 4 to 10. Therefore,

PICE-10 has the lowest T_g among these three kinds of PICEs for it has a more flexible polymer chain. No melting peaks are observed in the second heating cycle under a cooling rate of 10 °C/min or even 5 °C/min. We suppose that the crystallization rate of PICEs is rather low, and therefore, annealing was applied to improve crystallization of PICEs. PICEs were first heated at 160°C in a wind drying oven until they melted completely, then they were quenched by liquid nitrogen to obtain amorphous samples. The amorphous samples are transparent and elastic at room temperature. They were cut into small pieces around 0.5 mm*0.5 mm. Then the samples were annealed at 80°C for a certain time and taken regularly during annealing for DSC tests. The DSC results (Figure 4) show that both PICE-4 and PICE-10 could crystallize slowly by annealing.
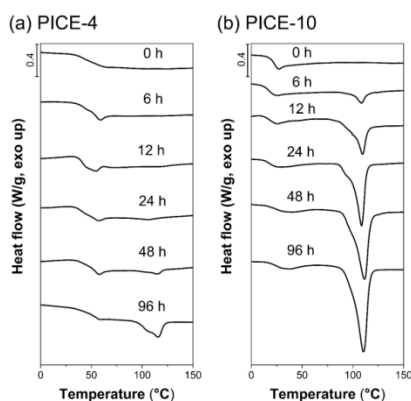

Figure 4 DSC curves of samples of PICEs with different annealing time: (a) PICE-4; (b) PICE-10. (1st heating cycle with a heating rate of 20 °C/min).

The T_m of PICE-4 is 116°C while the one of PICE-10 is 110°C after annealing for 96 h, which is much higher than the one of the typical aliphatic polyesters poly(ε-caprolactone) (around 60°C). Two melting peaks could be observed of PICE-4 and PICE-10, which indicates that there are different crystallites exist. Furthermore, since the length of alkane groups of PICE-10 is longer, the polymer chain is more flexible so that it can crystallize faster than PICE-4. In addition, it is found that the amorphous samples of PICE-10 would generally become rigid and opaque after a few days, which means crystallization occurred even at the room temperature, but this phenomenon does not happen when they were stored in the refrigerator at 5°C. That is because PICE-10 has a relatively lower T_g around room temperature due to its more flexible polymer chain, it can adjust the regularity of polymer chain at room temperature, which is beneficial to crystallization. But when the

temperature is below its T_g, the polymer chain is frozen and the material remains amorphous.

However, the samples of PICE-6 remained elastic and transparent after annealing at 60°C, 80°C or 100°C for 96 h, and no melting peak was observed from the DSC results, which indicates that PICE-6 crystallized extremely slowly to be observed.

3.3 Flame Retardancy

As mentioned above, PICEs are supposed to have outstanding flame retardancy due to the isocyanurate ring structure. Their limiting oxygen indexes (LOI) were measured to estimate their flammability. The higher LOI value represents better flame retardancy [39]. According to GB/T2406.2-2009 and GB/T8624-2012, when LOI≥32%, the building materials used as plastic conduit pipes or textiles are classified as class B1 (low flammability) while the class B2 (moderately flammability) requires LOI≥26%. The LOI data of PICEs are shown in Table 2. It is clear that both PICE-4 (LOI: 40.1%) and PICE-6 (31.4%) show remarkable flame retardancy without adding any flame retardant. The LOI values are outclass the common polyesters such as PBT (22%) [25] and PLA (23%) [26]. The LOI value of PICE-10 (22.8%) is obviously less than PICE-4 and PICE-6, since the longer alkane groups which means lower proportion of the isocyanurate moieties, decreases the fire resistance of the material. For further study of flame retardancy of PICEs, the vertical burning test is used to evaluate their practical flammability according to UL 94. The results are also shown in Table 2. PICE-6 reaches V-1 rating since all the samples extinguished as soon as the pilot flame removed and their drips were not inflamed. It is surprised that PICE-10 also reaches V-2 rating for the samples extinguished in about 25 s after the removal of pilot flame, but their drips were inflamed. PICEs show remarkable flame retardancy in varying degrees without adding any flame retardants. They are potential to be applied as flame-retardanted materials or used as flame retardants.

Table 2 Flammability of the PICEs.

	PICE-4	PICE-6	PICE-10
Limiting Oxygen Index (LOI, %)	40.1	31.4	22.8
UL 94	n. d.[a]	v-1	v-2

[a]   n. d.=not determined.

4 CONCLUSIONS

A series of renewable linear polyesters, polyisocyanuratoesters (PICEs), are designed and synthesized successfully from urea-based monomer bis (2-carbomethoxyethyl) isocyanurate and aliphatic diols. The thermal properties of PICEs were studied and it is found that isocyanurate linkages can improve the thermal stability of polyesters and all PICEs exhibit similar degradation behavior and regular glass transition among 22°C-45°C. The crystallization rate T_m of PICEs is slow. PICE-4 and PICE-10 can crystallize slowly by annealing at 80°C while PICE-6 cannot be observed to crystallize even by annealing. Both PICE-4 and PICE-6 show satisfied flame retardancy that they have high limiting oxygen index value, and PICE-6 and PICE-10 reaches V-1 and V-2 rating in UL 94. They are potentially used as flame retardanted materials. There may be more special features of PICEs, and further investigation of PICEs is underway in our group.

ACKNOWLEDGEMENTS

REFERENCES

1. M. Dunky, Urea-formaldehyde (UF) adhesive resins for wood. *Indian Journal of Adhesion* **18**, 95-107 (1998).

2. A. N. Rollinson, J. Jones, V. Dupont and M.V. Twigg, Urea as a hydrogen carrier: A perspective on its potential for safe, sustainable and long-term energy supply. *Energy & Environmental Science* **4**, 1216-1224 (2011).

3. J.F.T. Berliner, Crystal urea: Industrial development and properties. *Journal of Industrial and Engineering Chemistry* **28**, 517-522 (1936).

4. R. Lan, J.T.S. Irvine and S. Tao, Ammonia and related chemicals as potential indirect hydrogen storage materials. *International Journal of Hydrogen Energy* **37**, 1482-1494 (2012).

5. R. Lan and S. Tao, Ammonia carbonate fuel cells based on a mixed NH4+/H+ ion conducting electrolyte. *ECS Electrochemistry Letters* **2**, F37-F40 (2013).

6. R. Zevenhoven, S. Eloneva and S. Teir, Chemical fixation of CO2 in carbonates: Routes to valuable products and long-term storage. *Catal Today* **115**, 73-79 (2006).

7. A. J. Meijer, W. H. Lamers and R. A. Chamuleau, Nitrogen metabolism and ornithine cycle function. *Physiological Reviews* **70**, 701-748 (1990).

8. M. G. Pillai, P. Simha and A. Gugalia, Recovering urea from human urine by bio-sorption onto microwave activated carbonized coconut shells: Equilibrium, kinetics, optimization and field studies. *Journal of Environmental Chemical Engineering* **2**, 46-55 (2014).

9. M. Ganesapillai, A. Venugopal, V. Ananthkrishna and N. Tapankrishna, Influence of process parameters on sorption capacity of microwave activated biosorbents for urea recovery from human urine: A comparative study. *Asia-Pacific Journal of Chemical Engineering* **10**, 438-449 (2015).

10. P. Simha and M. Ganesapillai, Ecological sanitation and nutrient recovery from human urine: How far have we come? A review. *Sustainable Environment Research* **27**, 107-116 (2017).

11. J. Lu, Y. Kitamura, K. Takisawa and W. Jiang, Development of a partial heating system to enhance bio-ammonia production and recovery by anaerobic digestion of nitrogen-rich wastewater: Effect of partial heating modules. *Chemical Engineering Journal* **262**, 973-979 (2015).

12. D. She, H. Yu, Q. Huang, F. Li and C. Li, Liquid-phase synthesis of cyanuric acid from urea. *Molecules* **15**, 1898-1902 (2010).

13. P. I. Kordomenos and J. E. Kresta, Thermal stability of isocyanate-based polymers. 1. Kinetics of the thermal dissociation of urethane, oxazolidone, and isocyanurate groups. *Macromolecules* **14**, 1434-1437 (1981).

14. P. I. Kordomenos, J. E. Kresta and K. C. Frisch, Thermal stability of isocyanate-based polymers. 2. Kinetics of the thermal dissociation of model urethane, oxazolidone, and isocyanurate block copolymers. *Macromolecules* **20**, 2077-2083 (1987).

15. P. M. Schaber, J. Colson, S. Higgins, D. Thielen, B. Anspach and J. Brauer, Thermal decomposition (pyrolysis) of urea in an open reaction vessel. *Thermochim Acta* **424**, 131-142 (2004).

16. R. S. Skowron and A. Balas, An overview of developments in poly(urethane-isocyanurates) elastomers. *Polymers for Advanced Technologies* **13**, 653-662 (2002).

17. K. Ashida and K. Iwasaki, Thermosetting Foams. *Handbook of Plastic Foams: Types, Properties, Manufacture and Applications*, William Andrew Publishing, Park Ridge (1995).

18. Y. He, M. Zhou, B. Wu, Z. Jiang and J. Nie, Synthesis and properties of novel polyurethane acrylate containing 3-(2-hydroxyethyl) isocyanurate segment. *Progress in Organic Coatings* **67**, 264-268 (2010).

19. W. J. Kauffman, Linear polyesters containing isocyanurate rings. *Journal of Polymer Science Part A: Polymer Chemistry* **12**, 1735-1743 (1974).

20. H. Otsuka and T. Endo, Poly(hemiacetal ester)s: new class of polymers with thermally dissociative units in the main chain. *Macromolecules* **32**, 9059-9061 (1999).

21. T. C. Frazier, E. D. Little and B. E. Lloyd, Isocyanurates. I. Some condensation reactions of cyanuric acid1. *Journal of Organic Chemistry* **25**, 1944-1946 (1960).

22. H. Yim, R. Haselbeck, W. Niu, C. Pujol-Baxley, A. Burgard, J. Boldt et al., Metabolic engineering of Escherichia coli for direct production of 1,4-butanediol. *Nature Chemical Biology* **7**, 445-452 (2011).

23. A. Zeng and W. Sabra, Microbial production of diols as platform chemicals: Recent progresses. *Current Opinion in Biotechnology* **22**, 749-757 (2011).

24. T. Buntara, S. Noel, P. H. Phua, I. Melian-Cabrera, J. G. de Vries and H. J. Heeres, Caprolactam from renewable resources: Catalytic conversion of 5-hydroxymethylfurfural into caprolactone. *Angewandte Chemie, International Edition* **50**, 7083-7087 (2011).

25. J. Tuteja, H. Choudhary, S. Nishimura and K. Ebitani, Direct synthesis of 1,6-hexanediol from HMF over a heterogeneous Pd/ZrP catalyst using formic acid as hydrogen source. *ChemSusChem* **7**, 96-100 (2014).

26. T. Buntara, S. Noel, P. H. Phua, I. Melian-Cabrera, J. G. de Vries and H. J. Heeres, From 5-hydroxymethylfurfural (HMF) to polymer precursors: Catalyst screening studies on the conversion of 1,2,6-hexanetriol to 1,6-hexanediol. *Topics in Catalysis* **55**, 612-619 (2012).

27. M. J. Diamond and T. H. Applewhite, Alkaline cleavage of hydroxy unsaturated fatty acids and derivatives. II 10-hydroxydecanoic acid from ricinoleates and 1,10-decanediol from ricmoleyl alcohol. *Journal of the American Oil Chemists' Society* **44**, 656-658 (1967).

28. T. Koppl, S. Brehme, D. Pospiech, O. Fischer, F. Wolff-Fabris, V. Altstadt et al., Influence of polymeric flame retardants based on phosphorus-containing polyesters on morphology and material characteristics of poly(butylene terephthalate). *Journal of Applied Polymer Science* **128**, 3315-3324 (2013).

29. N. A. Isitman, M. Dogan, E. Bayramli, and C. Kaynak, The role of nanoparticle geometry in flame retardancy of polylactide nanocomposites containing aluminium phosphinate. *Polymer Degradation and Stability* **97**, 1285-1296 (2010).

30. I. P. Romanova, G. G. Yusupova, A. A. Nafikova, V. I. Kovalenko and O. G. Sinyashin, Synthesis of a single isomer of the bis-adduct of isocyanurato-substituted azide with [60] fullerene. *Russian Chemical Bulletin* **51**, 1491-1496 (2002).

31. X. Cui, X. Dai, Y. Deng and F. Shi, Development of a general non-noble metal catalyst for the benign amination of alcohols with amines and ammonia. *European Journal of Chemistry* **19**, 3665-3675 (2013).

32. G. Guillena, D. J. Ramon and M. Yus, Hydrogen autotransfer in the N-alkylation of amines and related compounds using alcohols and amines as electrophiles. *Chemical Reviews* **110,** 1611-1641 (2010).

33. S. Bahn, S. Imm, L. Neubert, M. Zhang, H. Neumann and M. Beller, The catalytic amination of alcohols. *ChemCatChem* **3**, 1853-1864 (2011).

34. R. N. Salvatore, C. H. Yoon and K.W. Jung, Synthesis of secondary amines. *Tetrahedron* **57**, 7785-7811 (2001).

35. I. C. McNeill and H. A. Leiper, Degradation studies of some polyesters and polycarbonates-1. Polylactide: General features of the degradation under programmed heating conditions. *Polymer Degradation and Stability* **11**, 267-285 (1985).

36. Y. Aoyagi, K. Yamashita and Y. Doi, Thermal degradation of poly[(R)-3-hydroxybutyrate], poly [ε-caprolactone], and poly[(S)-lactide]. *Polymer Degradation and Stability* **76**, 53-59 (2002).

37. I. C. McNeill and H. A. Leiper, Degradation studies of some polyesters and polycarbonates: 3-Polyglycollide. *Polymer Degradation and Stability* **12**, 373-385 (1985).

38. S. V. Levchik and E. D. Weil, A review on thermal decomposition and combustion of thermoplastic polyesters. *Advances in Polymer Technology* **15**, 691-700 (2004).

39. J. Troitzsch, *Plastics Flammability Handbook: Principles, Regulations, Testing, and Approval 3re Edition*, Hanser Verlag, Munich (2004).